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VIS–NIR spectroscopy as a process analytical technology for compositional characterization of film biopolymers and correlation with their mechanical properties

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ABSTRACT

There is an increasing interest in the use of polysaccharides and proteins for the production of biodegradable films. Visible and near-infrared (VIS–NIR) spectroscopy is a reliable analytical tool for objective analyses of biological sample attributes. The objective is to investigate the potential of VIS–NIR spectroscopy as a process analytical technology for compositional characterization of biodegradable materials and correlation to their mechanical properties. Biofilms were produced by single-screw extrusion with different combinations of polybutylene adipate-co-terephthalate, whole oat flour, glycerol, magnesium stearate, and citric acid. Spectral data were recorded in the range of 400–2498 nm at 2 nm intervals. Partial least square regression was used to investigate the correlation between spectral information and mechanical properties. Results show that spectral information is influenced by the major constituent components, as they are clustered according to polybutylene adipate-co-terephthalate content. Results for regression models using the spectral information as predictor of tensile properties achieved satisfactory results, with coefficients of prediction (R^2_C) of 0.83, 0.88 and 0.92 (calibration models) for elongation, tensile strength, and Young's modulus, respectively. Results corroborate the correlation of NIR spectra with tensile properties, showing that NIR spectroscopy has potential as a rapid analytical technology for non-destructive assessment of the mechanical properties of the films.

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1. Introduction

Plastic materials present several advantages such as being chemically and mechanically resistant, lightweight, heat-sealable, can be printed on and are available in large quantities at low cost, thus been widely used as food packaging. However, synthetic plastic materials are derived from non-renewable sources such as petroleum, and most of them are not biodegradable. Thus, they are environmentally harmful and their use has been restricted to avoid ecological damages [1]. The problems caused by discarding non-biodegradable materials have led to the research and development of biodegradable materials with characteristics that allow for their use in the production of packaging on a commercial scale. Biopolymers such as polysaccharides and proteins are available in large amounts from renewable sources [2]. There is an increasing interest in the use of biopolymers that could minimize the environmental impact of synthetic plastics. Starch-based materials stand out among the ones obtained from renewable sources, being used in the production of biodegradable materials such as films and sheets [3]. However, the drawbacks of starch-based materials include poor mechanical properties and high hydrophilicity. Several studies have proposed the addition of protein, fiber, or lipids to improve these properties but they were unable to achieve satisfactory results.

Determination of mechanical properties of film polymers requires destructive and time consuming methods, and is carried out in specific equipment such as texturometers by specialized analysts [4,5]. Thus, large scale production of films requires fast and non-invasive analytical methods in order to assess film composition and mechanical properties. Visible and near-infrared (VIS–NIR) spectroscopy is a well-established alternative as a non-destructive process analytical technology for measuring constituents of biological materials. The NIR spectrum is influenced by the different vibrational modes of the molecules, which are caused by their interaction with electromagnetic radiation absorbed at specific wavelengths. This technique has been used for the identification of several complex components such as proteins and carbohydrates in biological materials. Chemometrics allows the extraction of relevant information contained in the spectra for the development of calibration

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models that allow the classification and prediction of the composition of organic samples [6].

Previous studies have investigated the application of infrared (IR) spectral information as a non-destructive analytical method for determining physical and mechanical properties of non-biodegradable polymers [7–10]. An early study by Orman and Schumann [11] compared NIR calibration methods for predicting protein, oil and starch contents in both whole and ground maize samples. They worked within the spectral range of 1100–2500 nm in reflectance mode, obtaining reliable models for ground samples. However, the results were not compared to the processed product composition obtained from the samples, requiring further studies on this field for practical applications.

Developing new materials is a slow and time demanding process, which requires several physical and chemical analyses in order to characterize their properties. The main objective is to investigate VIS–NIR spectroscopy as a process analytical technology for compositional characterization of biodegradable materials and correlation to their mechanical properties. To our knowledge, no previous work has reported correlations of mechanical properties with spectral information in the NIR region. The specific objectives were the: (a) production of biodegradable materials with different compositions; (b) measurements of mechanical properties by traditional methods; (c) acquisition of spectral information in VIS–NIR spectral range; (d) application of multivariate statistical models to relate spectral information with chemical composition and mechanical properties, and (e) identification of most significant wavelengths associated with physicochemical and mechanical attributes of the samples.

2. Materials and methods

2.1. Biofilm production and visualization

The following components were used to produce the films: polybutylene adipate-co-terephthalate (PBAT) Ecoflex-F® (BASF, Germany), whole oat flour (WOF) (SL Alimentos Ltda, Brazil), technical grade glycerol (GLY) (Dinâmica, Brazil), magnesium stearate (MS) (Sigma-Aldrich, Germany) and citric acid (CA) (Sigma-Aldrich, Germany). The components of the formulation (WOF, PBAT, GLY, MS, and CA) were mixed manually at room temperature. The blend was extruded in a single-screw extruder (model EL-25, BGM, Brazil) with a screw diameter of $D = 25$ mm and a screw length of 28D, in order to produce pellets of 24 different blends (Table 1). A scanning electron microscope (SEM) (FEI Quanta 200, Japan) was used to acquire the surface and cryogenic fracture microstructures of the samples, in order to assess the homogeneity of the blends. Previously, the dried samples were coated in gold using a sputter coater (BALTEC SCD 050, Liechtenstein). Fig. 1 shows the fracture micrographs of the films. There was no significant phase separation between the components, and particles on the surface were non-gelatinized starch granules. The micrographs support the conclusion that the extrusion was efficient in producing a homogeneous blend of PBAT/WOF/GLY.

2.2. Mechanical properties

Mechanical tensile properties were determined according to the American Society for Testing and Materials (ASTM) D882-02 method [4], and the slow rate penetration resistance (SRPR) method according to ASTM F1306-90 [5], using a texturometer (Stable Micro Systems, model TA.XT2i, UK). Before the analyses, the samples were conditioned in glass desiccators for 48 h with a saturated solution of $MgNO_3$ at 23.0 ± 2.0 °C. The tensile properties measured were tensile strength (in MPa), elongation at break (in %), and Young's modulus (in MPa), and the slow rate penetration resistance properties measured were force to perforation (in MPa) and elongation to perforation (in %).

2.3. Spectra acquisition and data analysis

Two samples per formulation were cut to fit the sampling cell (width: 35 mm and length: 150 mm). Spectral data were collected in reflectance mode and recorded as absorbance ($\log 1/R$) with the XDS NIR XM 1100 Rapid Content Analyser (Foss NIRSystems, Denmark) using a rectangular cell, over the wavelength range of 400–2498 nm at 2 nm intervals. Between acquisitions, the cell analytical surface was washed with ethanol (70% v/v), rinsed with distilled water, and dried using a soft paper tissue.

Principal component analysis (PCA) is a commonly used exploratory tool of the spectral data structure, in which the data are projected into a subspace that minimizes the reconstruction error in the mean squared sense [12]. PCA was carried out to investigate the major influence of different factors in the spectral information. The matrix expression of the PCA model for the spectral data is $A = SV + E$, where A is the matrix of the spectral information ($n \times w$), S is the score matrix ($n \times p$), V is the eigenvector matrix ($p \times w$), E is a residual matrix ($n \times w$), n is the number of samples, w is the number of wavelengths, and p is the number of principal components [13]. The principal component (PC) scores and loadings indicate the information hidden in the spectra, and the wavelengths responsible for the most relevant information.

Partial least squares regression (PLSR) relates a set of independent variables used as predictors (wavelengths) with the response variables (observations) by reducing a large number of original predictors to a new uncorrelated set based on small number of orthogonal factors called latent variables [14]. PLSR was applied to the centered spectral datasets (1050 bands) for establishing independent models and finding relationship between spectra and mechanical properties of the biodegradable materials. In addition, the main regression coefficients are indicative of the most important wavelengths. PLS models were built using a training set under full cross validation by utilizing the leave-one sample-out cross-validation method (LOOCV). Prediction results using raw spectra were compared with those resulting from the spectral dataset after treatment with different pre-processing methods (SNV,

Table 1
Concentrations of whole oat flour (WOF), poly (butylene adipate-co-terephthalate) (PBAT), glycerol (GLY), citric acid (CA), and magnesium stearate (MS) used to produce the biodegradable materials. Numbers are expressed as g/100 g of mixture.

Formulation	WOF	PBAT	GLY	CA	MS	Formulation	WOF	PBAT	GLY	CA	MS
F1	30.0	40.0	29.48	0.02	0.5	F13	40.0	30.0	29.50	0.00	0.5
F2	30.0	40.0	29.50	0.00	0.5	F14	40.0	30.0	29.98	0.02	0.0
F3	30.0	40.0	30.00	0.00	0.0	F15	40.0	30.0	30.00	0.00	0.0
F4	32.5	40.0	26.98	0.02	0.5	F16	40.0	30.0	29.98	0.02	0.0
F5	32.5	40.0	27.00	0.00	0.5	F17	42.5	30.0	26.98	0.02	0.5
F6	32.5	40.0	27.48	0.02	0.0	F18	42.5	30.0	27.00	0.00	0.5
F7	32.5	40.0	27.50	0.00	0.0	F19	42.5	30.0	27.48	0.02	0.0
F8	35.0	40.0	25.00	0.00	0.0	F20	42.5	30.0	27.50	0.00	0.0
F9	35.0	40.0	24.50	0.00	0.5	F21	45.0	30.0	24.48	0.02	0.5
F10	35.0	40.0	24.98	0.02	0.0	F22	45.0	30.0	24.50	0.00	0.5
F11	35.0	40.0	24.48	0.02	0.5	F23	45.0	30.0	24.98	0.02	0.0
F12	40.0	30.0	29.48	0.02	0.5	F24	45.0	30.0	25.00	0.00	0.0

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